

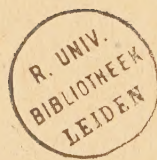
Thermal Cracking of Petroleum

By
H. C. Sung

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Thermal Cracking of Petroleum

EFFECT OF TIME, TEMPERATURE, PRESSURE, AND TYPE OF CHARGING STOCK ON PRODUCTS

H. C. SUNG, G. G. BROWN, AND R. R. WHITE

University of Michigan, Ann Arbor, Mich.

THE important variables in the thermal cracking of petroleum are time, temperature, pressure, and type of charging stock. The effect of these variables on the distribution and type of product obtained by the decomposition of close-cut fractions into gas, gasoline, coke, and other fractions is important in establishing the type of decomposition and polymerization reactions that occur. The design and efficient operation of thermal cracking units are based upon the rates at which these reactions proceed.

The apparatus and procedure were described previously (5) and shown to give results which are well within the range of accuracy required for the design and operation of thermal cracking units. The apparatus consisted of two bombs fitted with the necessary transfer lines, valves, and fittings. The bombs were immersed in a molten salt bath (50% potassium nitrate and 50% sodium nitrate), brought to the desired temperature before the charge was introduced. At the start of a run, bomb 1 was filled with molten solder and bomb 2 with nitrogen. The oil was charged to bomb 1. The pressure in bomb 1 was controlled by releasing solder from bomb 1 to bomb 2 through a manually controlled throttle valve. The increase in volume in the cracking zone of bomb 1 was followed by measuring the nitrogen displaced from bomb 1. At the end of a run, all of the products were displaced from bomb 1 by solder, expanded to low pressure, and cooled to about 60° F. The uncondensed vapors were metered and passed over activated charcoal in order to recover light gasoline fractions. The coke was scraped from the bomb and weighed.

The physical properties of the three charging stocks used are shown in Table I. Charging stock 1 was a Pennsylvania combined feed, obtained from a commercial cracking plant and containing about 75% of recycled material. This was the charging stock used by Huntington and Brown (5). Charging stocks 3 and 4 were close-cut fractions from a virgin mid-continent crude oil.

The results are summarized in Table II. The effective time at the cracking temperature was calculated from the actual time-temperature curves on the basis that the cracking rate doubles for each 18° F. temperature increase. It was found later that the cracking rate for the formation of gas, coke, and gasoline and coke actually doubled for a 19–22° F. increase for charging stock 1 and for a 20.7–24.3° increase for charging stocks 3 and 4. Since the actual cracking temperature fluctuated both above and below the indicated reaction temperature during the run, the

Experimental data on the thermal cracking of industrial combined-feed and virgin close-cut fractions have been obtained. The effect of time, temperature, pressure, and type of charging stock on the distribution and type of product and on the rates of the reactions involved has been evaluated from these results. Specific rates of reaction for the decomposition of the close-cut fractions for the production of gas and light distillate oils of various end points have been calculated. The specific polymerization rates of gas and gasoline have been determined, as well as qualitative information on the rate of formation of coke. The application of these data to commercial operations is indicated.

equivalent times reported in Table II are within the experimental accuracy, and no second correction was applied to the data.

The term "gasoline" in Table II refers to the products boiling below 390° F. in a column distillation plus the light gasoline fractions recovered by charcoal from the uncondensed vapor products. This "gasoline" corresponds to a raw refinery gasoline having an A.S.T.M. end point of 390° F.

The apparent loss due to retention of material in the lines and to handling was prorated among all of the products recovered on a weight basis.

EFFECT OF TIME AND TEMPERATURE

The effect of time and temperature on the yields of various products is shown in Figures 1, 2, and 3. Where numerals only are used to represent the experimental points, the points are at the center of the numerals. When both letters and numerals are used, the points are at the center of the letters. The slopes of these curves are proportional to the rates of production of the various products.

The material collected after each run may be classified into three groups: (a) the ultimate products of the cracking reactions, gas and coke; (b) the intermediate products which boil in the ranges between the boiling range of the ultimate products and that of the original charge; and (c) the material boiling within the boiling range of the charge.

The yields of gas and coke increase with time. The rate of gas production is high initially and decreases with time. The rate of coke formation is initially zero, increases slowly with time, and finally decreases upon prolonged heating. Both the yields and rates of production of gas and coke increase with temperature.

The yields of all intermediate products increase from zero to a maximum value and then decrease with increasing time. The rate of production of the intermediate products decreases to a maximum negative value (maximum rate of disappearance) and finally approaches zero with increasing time. This is attributable to the fact that these products are themselves cracked to gas and, to a lesser extent, polymerized or condensed to light residues. Thus, the yields decrease as cracking is continued beyond a certain time at which the rate of production is equal to the rate of disappearance by decomposition and polymerization. Higher temperatures increase the rate of all reactions, giving a sharper peak in the yield curves.

The yields, and the rate of disappearance of the fractions boiling within the boiling range of the original charge, decrease with increasing time as the result of an increasing resistance to cracking and, to a limited extent, of production by secondary reactions of new material in this boiling range. An increase in temperature increases the rate of disappearance of these fractions.

TABLE I. PHYSICAL PROPERTIES OF CHARGING STOCKS

Charging Stock No.	1	3	4
Gravity at 60° F., °A.P.I.	24.8	35.3	31.5
Column distillation, ° F.			
Initial b.p.	180	421	444
10% over	400	525	609
30%	452	540	634
50%	507	551	635
70%	574	567	665
90%	673	593	700

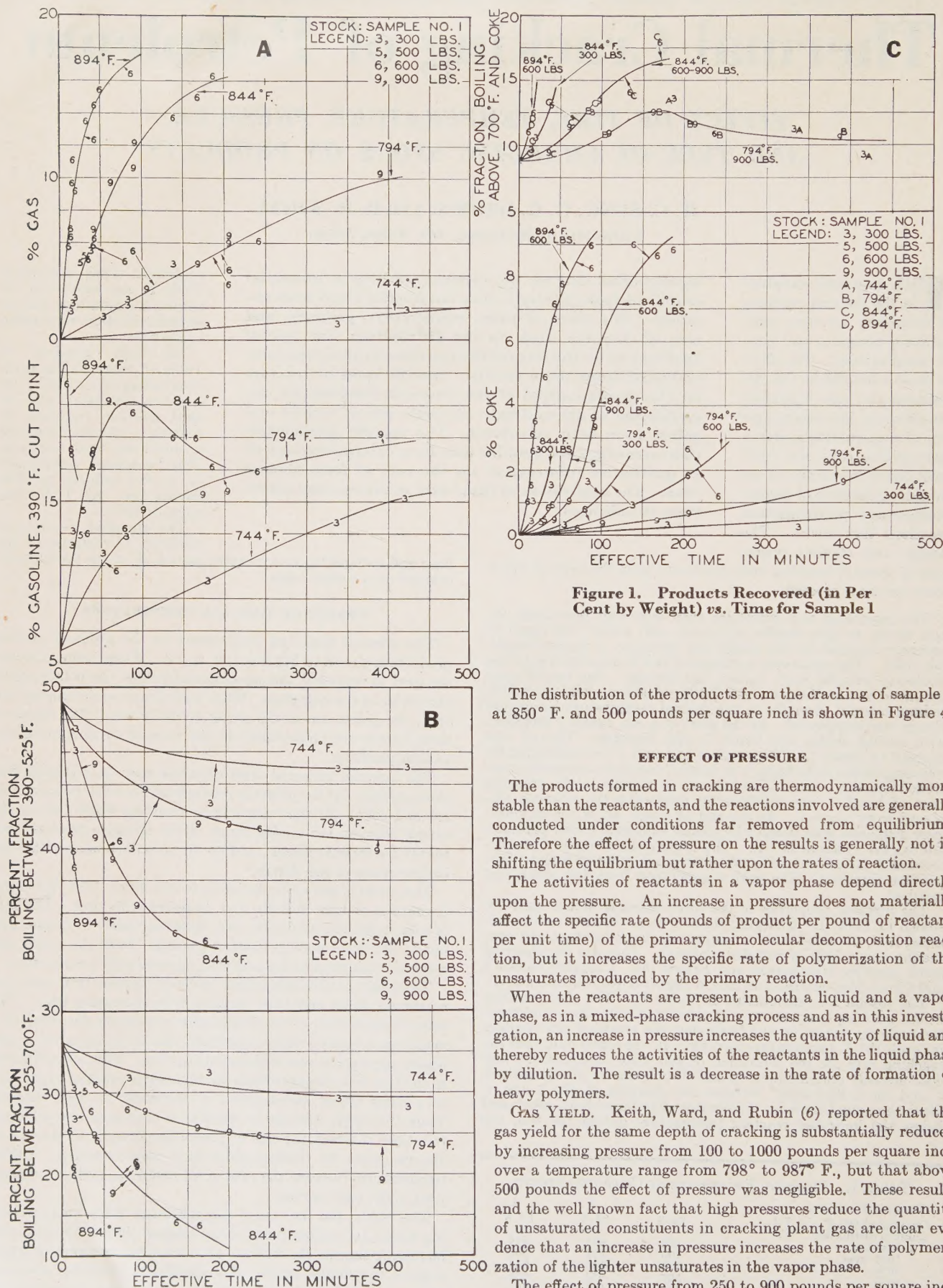


Figure 1. Products Recovered (in Percent by Weight) vs. Time for Sample 1

The distribution of the products from the cracking of sample 3 at 850° F. and 500 pounds per square inch is shown in Figure 4.

EFFECT OF PRESSURE

The products formed in cracking are thermodynamically more stable than the reactants, and the reactions involved are generally conducted under conditions far removed from equilibrium. Therefore the effect of pressure on the results is generally not in shifting the equilibrium but rather upon the rates of reaction.

The activities of reactants in a vapor phase depend directly upon the pressure. An increase in pressure does not materially affect the specific rate (pounds of product per pound of reactant per unit time) of the primary unimolecular decomposition reaction, but it increases the specific rate of polymerization of the unsaturates produced by the primary reaction.

When the reactants are present in both a liquid and a vapor phase, as in a mixed-phase cracking process and as in this investigation, an increase in pressure increases the quantity of liquid and thereby reduces the activities of the reactants in the liquid phase by dilution. The result is a decrease in the rate of formation of heavy polymers.

GAS YIELD. Keith, Ward, and Rubin (6) reported that the gas yield for the same depth of cracking is substantially reduced by increasing pressure from 100 to 1000 pounds per square inch over a temperature range from 798° to 987° F., but that above 500 pounds the effect of pressure was negligible. These results and the well known fact that high pressures reduce the quantity of unsaturated constituents in cracking plant gas are clear evidence that an increase in pressure increases the rate of polymerization of the lighter unsaturates in the vapor phase.

The effect of pressure from 250 to 900 pounds per square inch on the gas yields obtained in this investigation is very slight, as shown in Figures 1A, 2A, and 3A, because the volume and weight

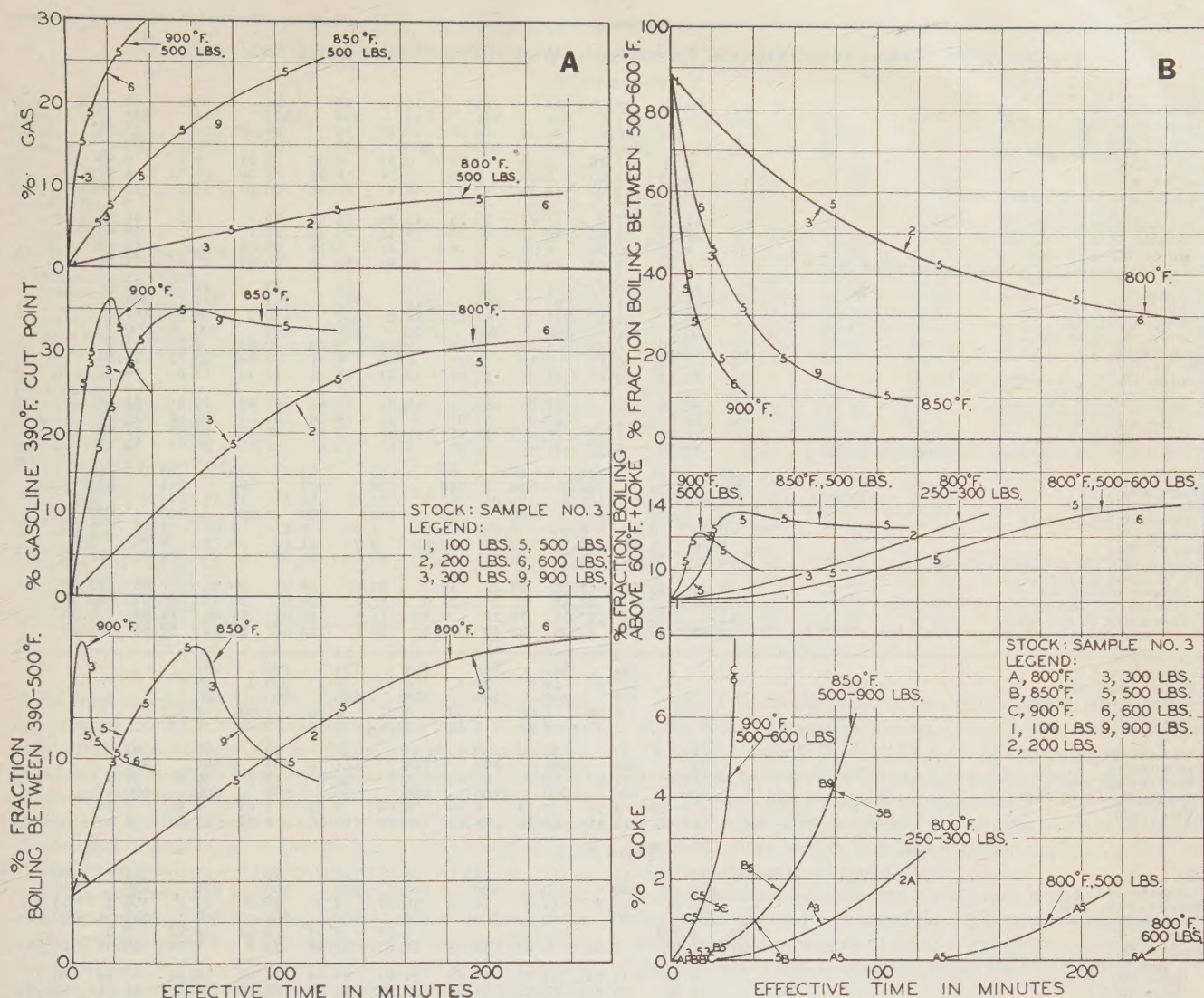


Figure 2. Products Recovered (in Per Cent by Weight) vs. Time for Sample 3

of the vapor relative to that of the liquid is small at pressures above 250 pounds. Keith, Ward, and Rubin reached this condition at higher pressures (above 500 pounds) because they operated at higher temperatures.

GASOLINE YIELD. The polymerization of the higher-boiling gasoline fractions probably occurs in the liquid phase, and an increase in pressure increases gasoline yield because it decreases gas yield and the polymerization of unsaturates in the gasoline boiling range.

HIGH-BOILING RESIDUE YIELD. The effect of pressure on the yields of heavy polymers and coke boiling above the range of the charging stock may be observed by examining the curves for 844° F. in Figure 1C, for 800° in Figure 2B, and for 800° in Figure 3B. In all cases an increase in pressure decreases the yield of the heavy polymer product for the same time and temperature.

COKE YIELD. The influence of pressure on coke yields is the same as on heavy polymer yield, as shown by the curves for 794° and 844° F. in Figure 1C, for 800° in Figure 2B, and for 800° and 850° in Figure 3B. The fact that the formation of coke is affected by pressure in the same manner as the formation of heavy polymers is consistent with the concept that coke formation is the final stage of successive polymerization and re-cracking, at least in a liquid- or mixed-phase cracking process for the production of gasoline.

CONVERSION

Reaction time, temperature, pressure, and the character of the charging stock are generally recognized as the independent variables which affect cracking. In commercial processes time and temperature are the major factors determining the extent to which the reactions are allowed to proceed before gas, gasoline, and residuum are separated from the cracking stock. For this reason the conversion (also called "depth of cracking") is used frequently to express the combined effect of time and temperature. The conversion is computed as the weight per cent yield of material boiling below the boiling range of the original charge. The conversion, as defined above, does not include the material boiling above the boiling range of the original charge formed by secondary reactions; but since the amount of this material is usually small, the conversion does indicate the extent of decomposition which has occurred.

An increase in temperature at constant pressure for the same conversion increases the proportion of lighter materials in the cracked products, and decreases the yield of heavy polymers and coke because the temperature coefficients for the cracking reactions which produce the lighter materials are greater than those for the polymerization reactions which produce the heavy polymers. Thus, increasing the temperature at constant pressure for the same conversion increases the amount of gas, and may or

TABLE II. RECOVERY OF PRODUCTS, EXPRESSED AS WEIGHT PER CENT OF TOTAL RECOVERY

SAMPLE No. 1										
Run number	Stock	12	15	16	18	19	21	22	23	
Temperature, ° F.	844	844	844	844	844	844	844	844	844	
Effective time, min.		16.37	39.33	15.06	41.27	40	88.47	186.2	35.77	
Pressure, lb./sq. in. gage		300	500	300	600	600	600	600	600	
Coke, wt. %	0.00	1.10	0.49	0.39	0.94	0.95	2.21	8.82	0.88	
Gas, wt. %	0.00	2.30	5.25	1.70	6.94	5.91	5.50	16.27	4.97	
Gasoline (390° F. cut point), wt. %	5.73	12.9	14.28	12.1	16.8	17.64	20.0	14.5	12.78	
Wt. % liquid boiling:										
Between 390° & 525° F.	49.17	47.4	31.47	46.13	45.35	35.66	41.7		40.52	
Between 525° & 700° F.	36.17	26.85	30.53	30.78	24.15	31.25	21.7		28.05	
Above 700° F. & coke	8.93	10.36	8.21	9.16	6.41	9.18	10.56		13.46	
Wt. % conversion into products boiling below 390° F.	0.00	9.66	14.06	8.2	18.36	18.18	20.31	27.81	12.24	
SAMPLE No. 2										
Run number	Stock	25	26	27	29	31	32	33	42	43
Temperature, ° F.	794	794	794	794	744	744	744	744	844	844
Effective time, min.	78.5	68.17	241.7	82.73	338.2	422	180.2	138.9	167.7	
Pressure, lb./sq. in. gage	600	600	600	300	300	300	300	600	600	
Coke, wt. %	0.79	0.23	1.24	1.69	0.24	0.59	0.33	9.0	8.6	
Gas, wt. %	4.96	0.73	6.13	2.45	0.98	1.97	0.94	13.71	14.88	
Gasoline (390° F. cut point), wt. %	13.11	10.67	16.59	12.67	12.94	15.15	10.11	17.0	16.77	
Wt. % liquid boiling:										
Between 390° & 525° F.	39.94		41.36	39.98	45.01	45.41	42.84	34.8	34.38	
Between 525° & 700° F.	28.0		24.9	32.0	29.25	28.26	32.65	14.15	13.95	
Above 700° F. & coke	13.76		10.62	12.71	11.07	9.1	13.43	18.34	17.83	
Wt. % conversion into products boiling below 390° F.	12.57	5.70	17.39	9.58	8.94	11.5	5.35	26.98	28.11	
SAMPLE No. 3										
Run number	Stock	45	46	48	50	51	53	54	55	56
Temperature, ° F.	794	794	794	844	844	844	844	894	894	794
Effective time, min.	205.8	102.6	167.8	92.05	40.5	61.03	15.5	15.14	392.5	9.6
Pressure, lb./sq. in. gage	900	900	900	900	900	900	600	600	900	600
Coke, wt. %	0.69	0.36	0.46	3.32	0.50	1.08	3.17	2.62	1.68	1.09
Gas, wt. %	5.96	3.18	4.58	12.19	6.85	9.71	11.15	9.73	10.33	5.8
Gasoline (390° F. cut point), wt. %	15.29	14.43	15.3	16.31	17.9	20.83	16.89	17.3	18.73	21.76
Wt. % liquid boiling:										
Between 390° & 525° F.	43.46	43.67	41.55	36.52	40.7	39.37	38.91	39.85	39.93	40.89
Between 525° & 700° F.	25.35	27.8	25.85	21.2	24.9	17.8	20.0	20.52	19.34	25.55
Above 700° F. & coke	11.6	10.79	12.51	13.12	9.36	11.8	12.04	11.66	11.09	5.54
Wt. % conversion into products boiling below 390° F.	13.86	12.01	14.36	23.43	19.31	25.3	23.32	22.24	23.91	22.29
SAMPLE No. 4										
Run number	Stock	9	13	14	17	24	28	30		
Temperature, ° F.	794	844	844	844	794	794	794	794		
Effective time, min.	137.4	17.8	39.5	25.38	55.2	205.1	82.7			
Pressure, lb./sq. in. gage	300	300	300	500	300	600	300			
Coke, wt. %	0.93	1.09	1.56	0.37	0.30	1.83	1.62			
Gas, wt. %	2.36	2.52	5.46	1.70	1.40	3.42	2.12			
SAMPLE No. 5										
Run number	Stock	35	37	38	39	44	49	59	60	61
Temperature, ° F.	894	894	894	894	794	844	894	894	894	894
Effective time, min.	51.0	87.0	42.2	41.7	204.9	89.0	13.1	30.8	18.8	
Pressure, lb./sq. in. gage	600	600	600	600	600	900	600	600	600	
Coke, wt. %	7.75	8.22	7.19	6.68	2.66	3.63	1.63	4.89	3.58	
Gas, wt. %	15.47	16.41	12.31	14.41	4.35	10.56	6.25	13.49	9.20	
SAMPLE No. 6										
Run number	Stock	11	12	13	14	15	16	33	34	35
Temperature, ° F.	800	800	850	900	900	850	850	850	850	850
Effective time, min.	67.9	229.3	19.8	10.12	30.27	72.3	35.2	21.3	104.3	55.4
Pressure, lb./sq. in. gage	300	600	300	300	600	900	500	500	500	500
Coke, wt. %	1.303				7.12	4.31	2.31	0.31	3.6	
Gas, wt. %	2.58	7.97	6.21	10.98	21.62	17.48	11.3	7.78	23.88	16.98
Wt. % gas + liquid boiling:										
Below 200° F.	8.45	17.21	13.67	19.83	31.91	29.34	21.92	15.57	36.19	29.91
Below 300° F.	15.53	30.40	23.63	31.52	39.12	43.09	33.86	24.58	48.21	42.03
Below 400° F.	25.2	41.55	34.63	40.4	50.55	51.54	43.58	31.48	58.22	53.06
Gasoline (390° F. cut point), wt. %	21.68	32.82	27.54	28.56	28.14	33.63	31.31	22.95	33.0	35.04
Wt. % liquid boiling:										
Between 390° & 500° F.	3.35	13.67	16.52	9.93	14.63	9.87	10.85	12.69	10.28	9.86
Between 500° & 600° F.	88.5	52.49	29.6	44.12	40.52	13.4	16.13	31.63	46.44	10.5
Between 600° & 700° F.	8.15	3.88	5.3	6.27	2.62	3.85	4.27	4.95	4.35	5.48
Above 600° F. & coke	8.15	9.57	13.09	12.2	5.31	26.97	21.91	13.07	12.55	12.76
Above 700° F. & coke		5.69	7.79	5.93	2.69	23.12	17.64	8.12	7.2	7.28
Wt. % conversion into products boiling below 390° F.	0.00	24.26	40.79	33.75	39.54	49.76	51.11	42.61	30.73	56.88
SAMPLE No. 7										
Run number	Stock	37	38	39	40	41	42	43	44	45
Temperature, ° F.	800	800	800	800	800	925	900	900	900	850
Effective time, min.	129.6	78.5	197.3	3.36	116.7	25.43	25.7	7.85	11.35	14.4
Pressure, lb./sq. in. gage	500	500	500	100	250	500	500	500	500	500
Coke, wt. %	7.35	5.04	8.85	0.44	5.39	6.87	1.28	1.04	1.61	5.46
Gas, wt. %	14.93	11.43	17.8	0.56	12.01	42.69	37.29	23.19	27.86	10.71
Wt. % gas + liquid boiling:										
Below 200° F.	23.68	17.72	27.44	0.66	19.2	52.19	50.06	34.63	39.45	18.68
Below 300° F.	35.04	24.3	39.31	0.86	27.23	59.55	59.69	43.01	50.02	24.3
Gasoline (390° F. cut point), wt. %	26.66	18.59	28.77	0.37	20.03	25.11	32.75	26.14	29.95	18.02
Wt. % liquid boiling:										
Between 390° & 500° F.	12.59	8.95	13.4	4.45	11.1	7.12	9.97	11.15	10.85	11.51
Between 500° & 600° F.	42.75	57.49	34.95	87.03	51.23	18.16	20.0	36.68	28.28	56.23
Between 600° & 700° F.	5.9	4.75	6.75	1.74	6.45	3.37	4.25	3.65	4.46	6.96
Above 600° F. & coke	10.65	9.93	14.03	7.71	12.25	15.77	11.24	10.64	11.83	8.78
Above 700° F. & coke	4.75	5.18	7.28	5.97	5.8	12.4	6.99	7.04	7.37	1.82
Wt. % conversion into products boiling below 390° F.	34.01	23.63	37.62	0.81	25.42	58.95	58.79	41.48	49.04	23.48

(Continued on page 1157)

may not increase the amount of gasoline produced, depending primarily upon the initial boiling point of the original charge. If the initial boiling point of the charge is well above the boiling range of the gasoline, an increase in temperature may increase the gasoline production; if the initial boiling point of the charge is within or near the gasoline boiling range, the gasoline production may be decreased because of the increased gas production. Thus with specified limits of coke and residuum production, it is

possible to increase the conversion at constant pressure by increasing the temperature of the operation.

TYPE OF CHARGING STOCK

Typical data showing the yields of gas, gasoline, coke, and heavy polymers for the same time, temperature, and pressure are summarized in Table III to show the difference between the

TABLE II. RECOVERY OF PRODUCTS, EXPRESSED AS WEIGHT PER CENT OF TOTAL RECOVERY (Continued)

	SAMPLE No. 4							
	Stock	19	20	21	22	24	25	30
Run number	...	800	800	850	900	800	900	850
Temperature, ° F.	...	114.9	97.9	23.2	14.43	241.2	25.24	36.47
Effective time, min.	...	300	300	300	300	900	900	300
Pressure, lb./sq. in. gage	...	...	1.72	2.07	2.59	3.45	10.36	1.42
Coke, wt. %	...	7.48	5.73	8.68	17.61	14.89	23.99	10.49
Gas, wt. %	...	...	...	...	...	...	...	...
Wt. % gas + liquid boiling:	...	...	...	...	...	...	...	...
Below 200° F.	...	13.81	14.91	15.01	28.18	22.29	34.6	20.15
Below 300° F.	...	22.67	18.55	24.77	40.51	33.53	46.12	31.22
Below 400° F.	0.00	32.89	26.25	32.93	49.67	43.74	54.07	40.37
Gasoline (390° F. cut point), wt. %	...	24.3	20.01	23.35	31.14	27.84	29.47	28.93
Wt. % liquid boiling:	...	...	...	...	...	...	...	...
Between 390° & 500° F.	0.15	11.24	10.99	12.04	9.3	14.16	8.73	12.62
Between 390° & 600° F.	6.08	21.15	22.16	24.99	17.47	24.96	15.34	23.2
Between 500° & 600° F.	5.93	9.91	11.17	12.95	8.17	10.8	6.61	10.58
Between 600° & 700° F.	83.92	24.04	26.90	26.91	19.01	16.8	9.54	22.62
Above 700° F. & coke	10.0	23.03	25.2	16.07	14.77	15.51	21.66	14.76
Wt. % conversion into products boiling below 390° F.	0.00	31.78	25.74	32.03	48.75	42.73	53.46	39.42
Run number	31	47	48	49	50	51	52	53
Temperature, ° F.	900	850	850	900	800	800	900	850
Effective time, min.	34.4	20.5	52.23	11.86	212.9	126.8	36.03	11.46
Pressure, lb./sq. in. gage	600	500	500	500	500	500	500	250
Coke, wt. %	9.22	...	1.52	4.75	1.96	...	7.15	...
Gas, wt. %	26.17	8.67	18.49	16.74	12.98	8.63	31.28	5.84
Wt. % gas + liquid boiling:	...	...	...	...	...	...	...	...
Below 200° F.	38.44	14.94	27.89	25.55	20.86	14.33	39.2	8.89
Below 300° F.	50.7	23.47	39.92	35.26	31.46	24.66	49.52	14.94
Below 400° F.	57.25	33.52	50.93	44.71	43.89	35.48	57.57	21.31
Gasoline (390° F. cut point), wt. %	30.48	24.05	31.57	27.06	29.99	25.28	25.72	14.71
Wt. % liquid boiling:	...	...	...	...	...	...	...	...
Between 390° & 500° F.	8.66	10.47	10.74	11.74	13.86	12.48	7.04	9.14
Between 390° & 600° F.	14.52	24.13	20.12	18.84	26.61	21.28	13.48	18.05
Between 500° & 600° F.	5.86	13.48	9.38	7.1	12.75	8.78	6.43	8.91
Between 600° & 700° F.	11.0	20.65	17.45	23.8	18.55	32.45	14.23	52.42
Above 700° F. & coke	15.83	22.81	12.87	13.56	11.87	12.38	15.3	8.98
Wt. % conversion into products boiling below 390° F.	56.65	32.72	50.06	43.8	42.97	33.91	57.0	20.55

yields from charging stocks 1, 3, and 4. Although the pressure for charging stock 1 is higher than for stocks 3 and 4, an approximate comparison of the yields can be made because the behavior of stock 1 differs widely from that of stocks 3 and 4. Table III shows that charging stock 1 cracks at a lower rate than either stocks 3 or 4, since the quantity of material remaining within the original boiling range of the stock is much greater and the yields of gas, gasoline, and heavy polymers are lower.

At the same gas plus gasoline yield (Table IV), the combined-feed charging stock 1 gives a higher yield of gas than the virgin charging stocks 3 and 4. This is confirmed by the results of other investigations (1, 13). The gas yield from the heavier charging stock 4 is greater than that from charging stock 3. Apparently at equal yields of gas plus gasoline, the heavier virgin material is more completely decomposed than the lighter virgin material. This is substantiated by the fact that less material remains within the original boiling range for charging stock 4 than for charging stock 3. From the point of view of maximum gasoline production with minimum gas production, light virgin charging stocks are the most suitable.

The coke yield from the partially cracked charging stock 1 is much larger than for either stock 3 or 4. Similar data have been obtained by others (1, 7, 13). This may be attributed to the unsaturated character of the cracked charging stock which results in greater polymerization in the liquid phase.

Table V shows the yields of coke from charging stocks 3 and 4 at the same temperature, pressure, and gas-plus-gasoline yield. These data indicate that the lighter virgin charging stock 3 produces more coke at the same gas-plus-gasoline yield, temperature, and pressure than the heavier virgin stock 4. This may be due to the presence of more material in the vapor phase of the lighter material, which results in a higher concentration of polymerizable unsaturates in the liquid phase.

The commercial significance of these data is that if light charging stocks are used because of their low gas yields, higher pressures should be employed in order to reduce the concentration of polymerizable unsaturates in the liquid phase to a minimum.

SPECIFIC REACTION RATES

DECOMPOSITION. Previous investigators (2, 5, 6, 7) correlated cracking rates by the unimolecular rate equation:

$$k = \frac{1}{t} \ln \frac{A_0}{A_0 - X} \quad (1)$$

where k = specific reaction velocity constant, reciprocal sec.

t = time, sec.

A_0 = original charging stock, lb.

X = charging stock decomposed at time t , lb.

The activation energies were computed from the Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \quad (2)$$

where k = reaction velocity constant

Q = activation energy

T = absolute temperature

R = gas constant

The values of k calculated from experimental data decrease with increasing conversion and, therefore, must be extrapolated to 0% conversion in order to obtain the true reaction velocity constant. Previous work evaluated the reaction velocity constants for the production of gas and gasoline. The results from charging stocks 3 and 4 of this investigation have been used to determine the reaction velocity constants for the production of gas and light distillates of various end points.

TABLE III. YIELDS OF PRODUCTS FROM CRACKING AT CONSTANT TIME, TEMPERATURE, AND PRESSURE

Sample No.	1		3		4	
Temperature, ° F.	844		850		850	
Pressure, lb./sq. in. abs.	600		300		300	
Boiling range of charging stock, ° F.	390-700		500-600		600-700	
Time, minutes	30	60	30	60	30	60
Yields, % by wt.						
Material in original boiling range	70.8	61.3	35.9	18.2	22.3	15.7
Gas	4.5	8.8	10.2	17.4	11.4	19.8
Gasoline	15.8	20.2	29.0	35.0	27.4	32.4
Gas and gasoline	20.3	29.0	39.2	52.4	38.8	52.2
Heavy polymers and coke	9.8	11.0	13.5	13.0	19.2	11.1
Coke	0.57	1.96	0.51	2.01	0.34	1.94
Coke + gasoline	0.0357	0.0973	0.0178	0.0575	0.0125	0.0598

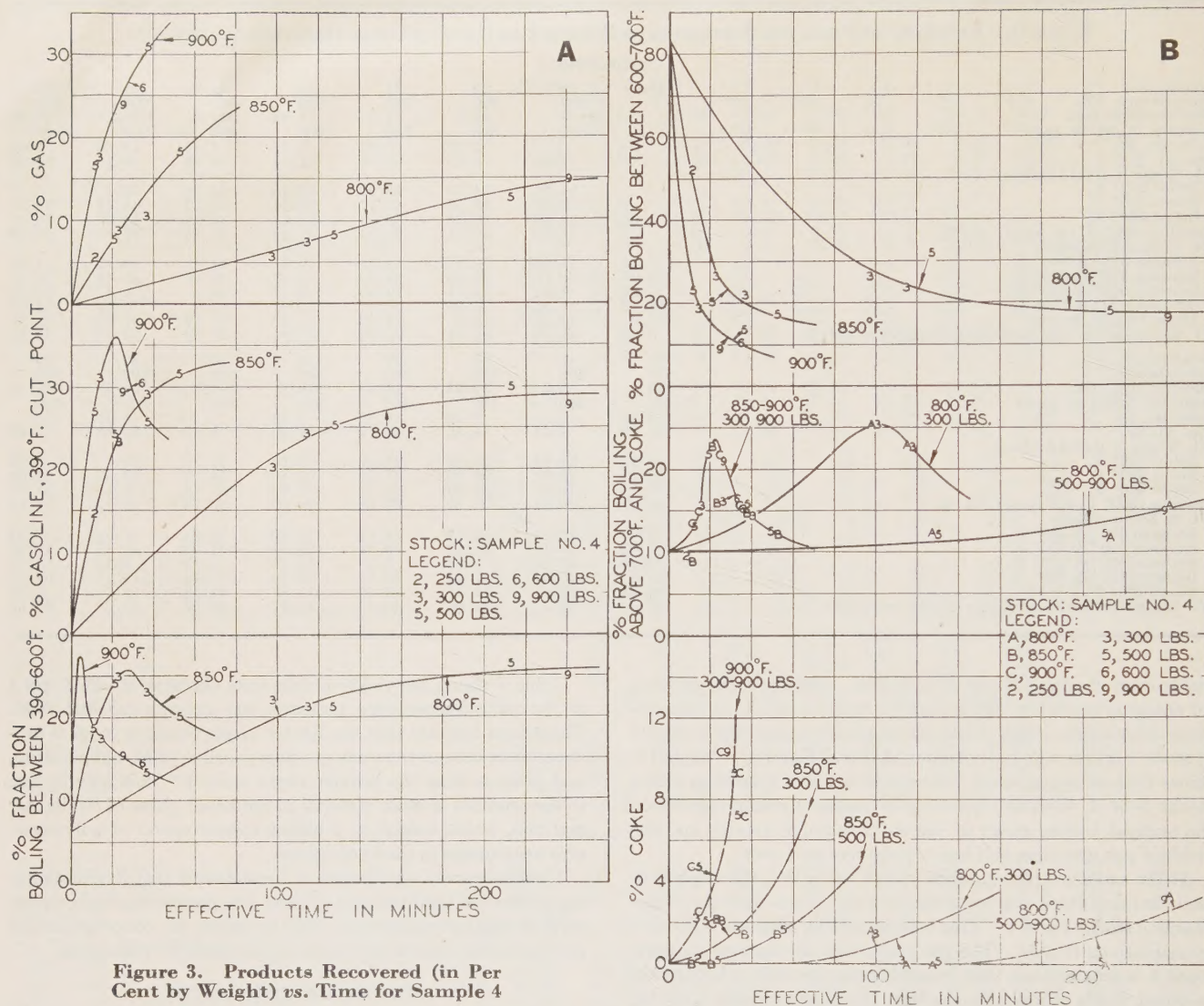


Figure 3. Products Recovered (in Per Cent by Weight) vs. Time for Sample 4

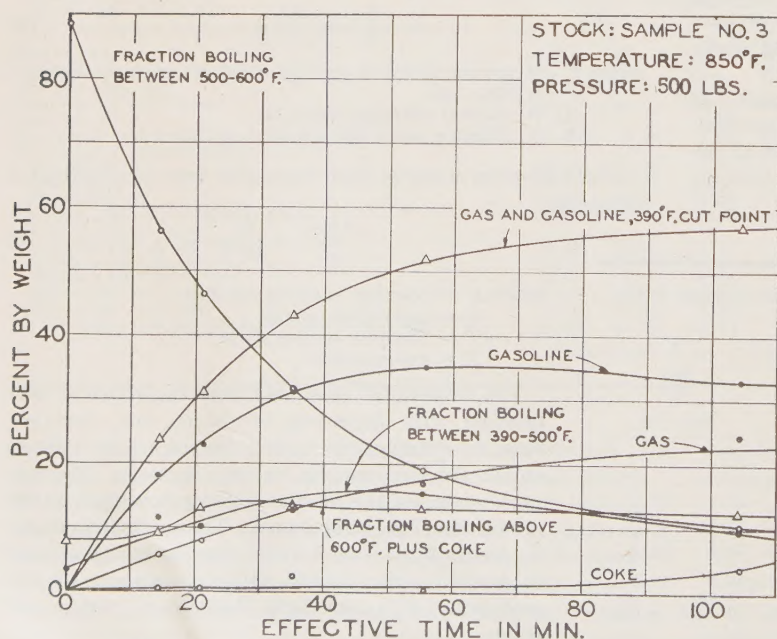


Figure 4. Effect of Time on Amount of Products

Figure 5 shows the calculated values of k as a function of per cent conversion to gas and distillates of specified end points and the extrapolation of these curves to 0% conversion. The reaction velocity constants for primary decomposition obtained from Figure 5 are plotted as a function of the reciprocal of absolute temperature in Figure 6. Figure 6 shows that the reaction velocity constant increases with the end point of the gas and distillate considered as a product.

Figure 7 compares the reaction velocity constant from this investigation for the production of gas and gasoline with the results of other investigators. All the velocity constants determined from liquid-phase cracking show identical slopes when plotted against reciprocal temperature, whereas those from vapor-phase cracking have a lower slope. This indicates that liquid-phase decomposition requires a greater energy of activation than vapor-phase decomposition.

Table VI shows the activation energy for primary decomposition into gas and distillate of various end points for charging stocks

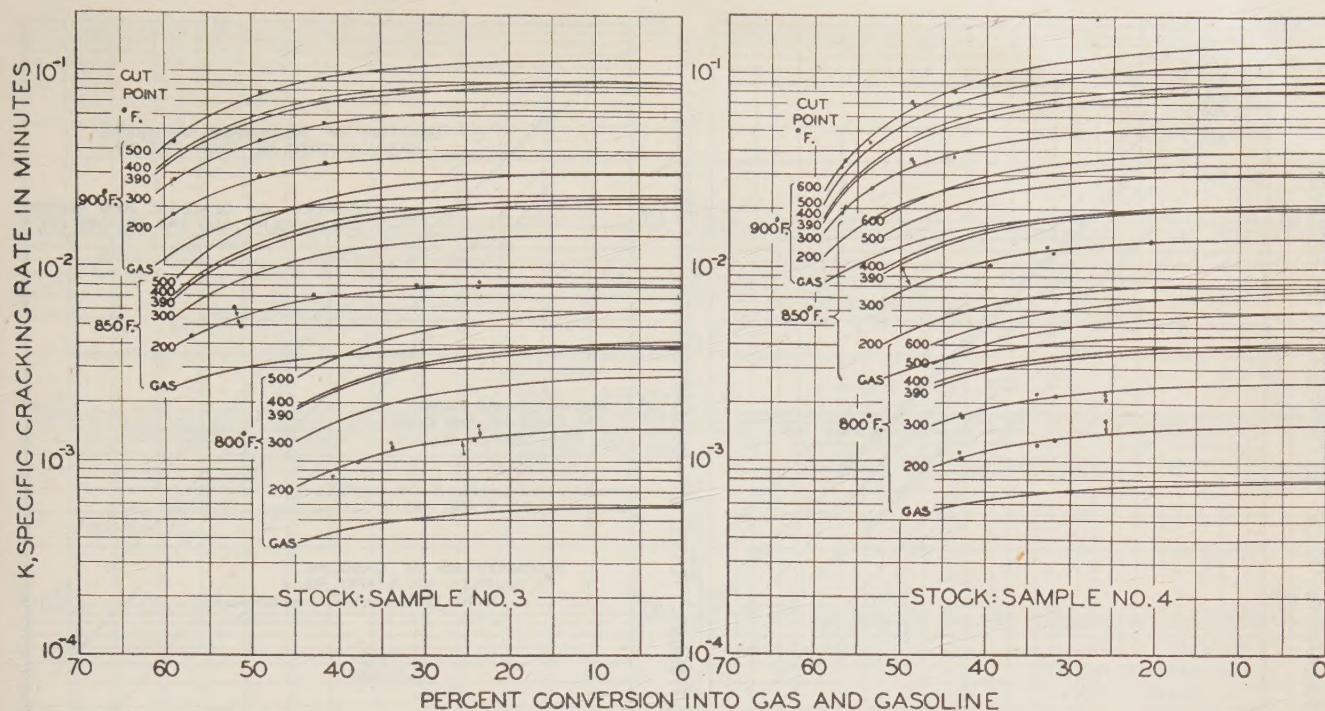


Figure 5. Variation in Specific Cracking Rate with Conversion

TABLE IV. YIELDS OF PRODUCTS FROM CRACKING AT CONSTANT TEMPERATURE, PRESSURE, AND GAS-PLUS-GASOLINE YIELD

Temperature, ° F.	844	850	850
Pressure, lb./sq. in. abs.	600	500	500
Charging stock No.	1	3	4
Yields, % by wt.			
Gas + gasoline	20	20	20
Gas	7.1	4.8	5.3
Gasoline	12.9	15.2	14.7
Gas + gasoline	0.382	0.316	0.360
Coke	1.6	0	0
Coke + gasoline	0.086	0	0

TABLE V. YIELDS OF COKE AND GASOLINE FROM CHARGING STOCKS 3 AND 4 AT 800° F.

Pressure, lb./sq. in.	Stock 3			Stock 4		
	300	500	500	300	500	500
Yields, % by wt.						
Gas + gasoline	20	30	40	20	30	40
Gasoline	15.8	23.6	30.8	15.6	23.0	28.9
Coke	0.45	0.50	1.60	0	0	1.5
Coke ÷ gasoline	0.0285	0.0212	0.0520	0	0	0.0519

3 and 4. The values indicate that higher activation energies are required for the production of lighter products. The activation energy for the destruction of a carbon-hydrogen linkage has been determined as 92,000 calories and that for a carbon-carbon linkage as 72,000 calories (9). Thus, higher activation energies for lighter products indicate either that a higher proportion of carbon-hydrogen rupture takes place in gas production, or that the formation of a smaller molecule requires a greater number of carbon-carbon ruptures. The activation energies for the production of gas and gasoline is 58,130 calories for charging stock 3 and 58,700 for charging stock 4. Other investigators obtained 57,100 calories (6) for the production of gas and gasoline, 59,200 calories (5) for gas, gasoline, and coke, and 53,400 calories (2) for gas, gasoline, and tar from vapor-phase cracking.

The relatively small difference between the activation energies from charging stocks 3 and 4 indicates that the activation

energies for the decomposition of all close-cut fractions from the same virgin crude oil are approximately equal.

SPECIFIC POLYMERIZATION RATES OF GAS AND GASOLINE. The decomposition and polymerization reactions that proceed during cracking may be represented diagrammatically as in Figure 8. It is apparent that the cracking process is not simple and that a rigorous treatment of the nine reactions shown is extremely difficult, if not impossible. Average polymerization reaction velocity constants for gas and gasoline may be evaluated by defining $G = L + V$ and by integrating Equation 3:

$$\frac{dG}{dt} = (K_1 + K_2)A_G - K_G G^2 \quad (3)$$

where G = weight % of gas + gasoline at time t
 K_G = polymerization reaction velocity constant for gas + gasoline, (lb. sec.)⁻¹
 A_G = weight % of material producing gas + gasoline at time t

The weight per cent of material producing gas and gasoline, A_G , may be evaluated if it is assumed: (1) The products heavier than gasoline, excluding those produced by polymerization of gas or gasoline, have the same decomposition velocity constants as the original charging stock; i.e., the effect of reaction $A \xrightarrow{K_3} P$ is negligible. (2) The products heavier than gasoline produced by the polymerization of gas and gasoline do not re-crack to gas and gasoline; i.e., the reactions $P \xrightarrow{K_4} V$ $P \xrightarrow{K_5} L$ are negligible. Thus,

$$\frac{-dA_G}{dt} = (K_1 + K_2)A_G \quad (4)$$

$$A_G = A_0 e^{-(K_1 + K_2)t} \quad (5)$$

where A_0 = weight % of original charge

Substituting the value of A_G given by Equation 5 in Equation 3 and writing in integral form:

$$G = (K_1 + K_2) A_0 \int_0^t e^{-(K_1 + K_2)t} dt - K_G \int_0^t G^2 dt \quad (6)$$

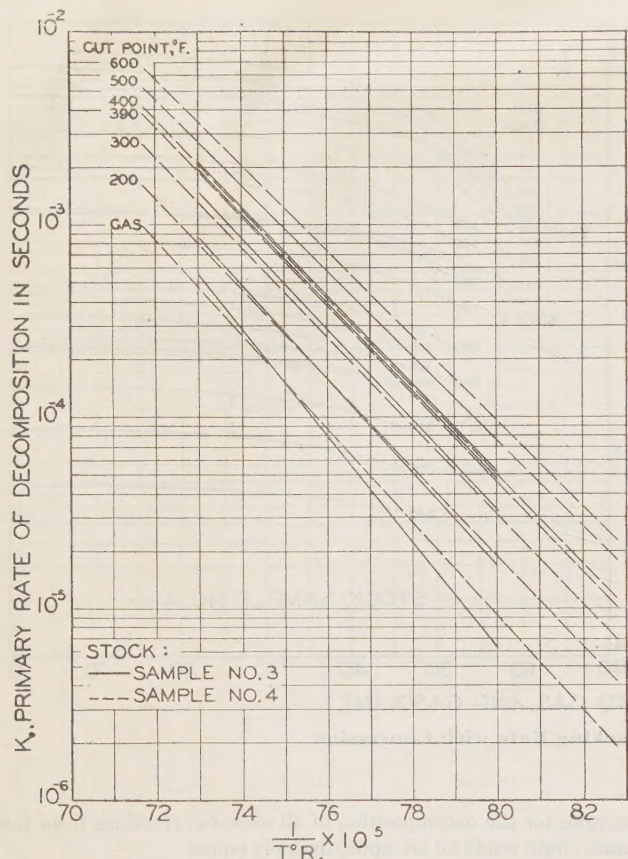


Figure 6. Primary Rate of Decomposition into Gas and Liquid Boiling below the Cut Point Indicated, as Affected by Temperature

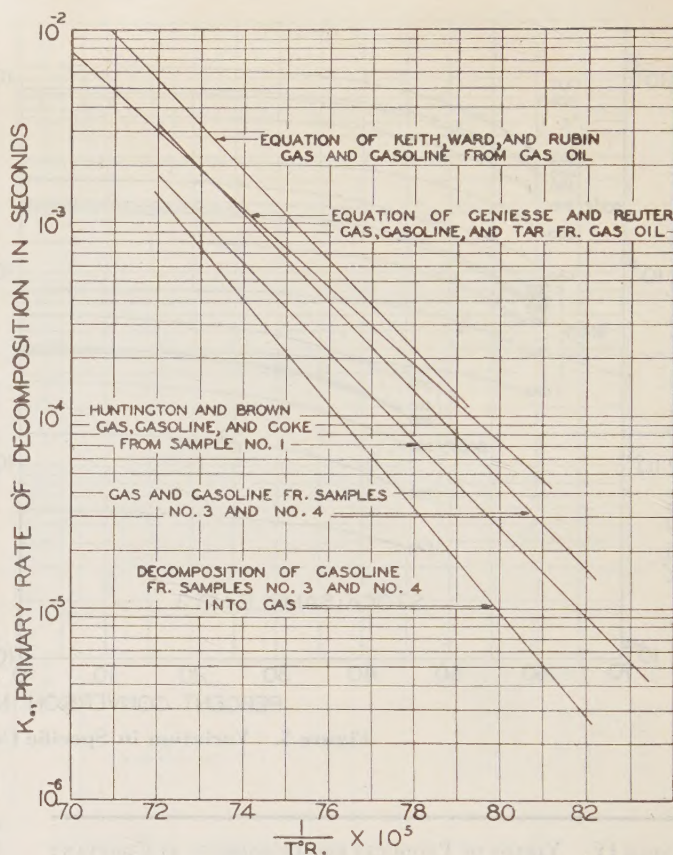


Figure 7. Primary Rate of Decomposition of Products Indicated, as Affected by Temperature

TABLE VI. ACTIVATION ENERGY FOR PRIMARY DECOMPOSITION INTO DISTILLATE PRODUCTS

Charging Stock No.	Gas	Calories/Gram Mole at Cut Point of:					
		200° F.	300° F.	390° F.	400° F.	500° F.	600° F.
3	70,500	61,700	59,900	58,130	58,300	55,850	
4	61,500	59,100	58,900	58,700	58,720	56,850	55,850

Furthermore, since the rate of polymerization of gas into fractions heavier than gasoline is probably negligible, the rate of polymerization of gas and gasoline is equal to the rate of polymerization of gasoline alone:

$$K_G G^2 = K_L L^2 \quad (7)$$

$$K_L = K_G \left(\frac{G}{L} \right)^2 \quad (7A)$$

Values of K_L were calculated from the experimental data by Equations 6 and 7A, and are plotted as a function per cent conversion to gas and gasoline in Figure 9. These curves show that the specific rate of polymerization of gasoline is low at low percentage conversions, increasing to a maximum and then decreasing with increasing percentage conversion. The rate of polymerization increases with increasing temperature and with decreasing pressure.

SPECIFIC DECOMPOSITION RATE OF GASOLINE. The reaction velocity constant K_4 (Figure 8) for the decomposition of gasoline to gas may be evaluated by a similar procedure. As before,

$$\frac{dV}{dt} = K_1 A_V - K_{VL} V^2 \quad (8)$$

where A_V = weight % of material producing gas

The weight per cent of material producing gas, A_V , may be evaluated if it is assumed that the products, excluding those

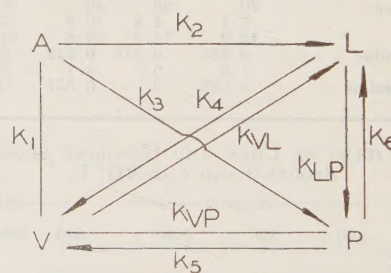


Figure 8. Diagram of Decomposition and Polymerization Reactions

A_0 = initial cracking stock, %
 A = initial cracking stock remaining, %
 L = gasoline, %
 V = gas, %
 P = polymerization and decomposition products boiling above end point of gasoline, %
 $G = L + V$
 $K_1, K_2, K_3, K_4, K_5, K_6$ = specific decomposition rates
 K_{VL}, K_{VP}, K_{LP} = specific polymerization rates

produced by gas polymerization, have the same decomposition velocity constants for gas production as the original charge, and that the products resulting from gas polymerization do not produce gas. Then,

$$A_V = A_0 e^{-K_1 t} \quad (9)$$

The rate of gas production is also given by the following equation:

$$\frac{dV}{dt} = K_1 A_0 e^{-K_1 t} + K_4 L - K_{VL} V^2 \quad (10)$$

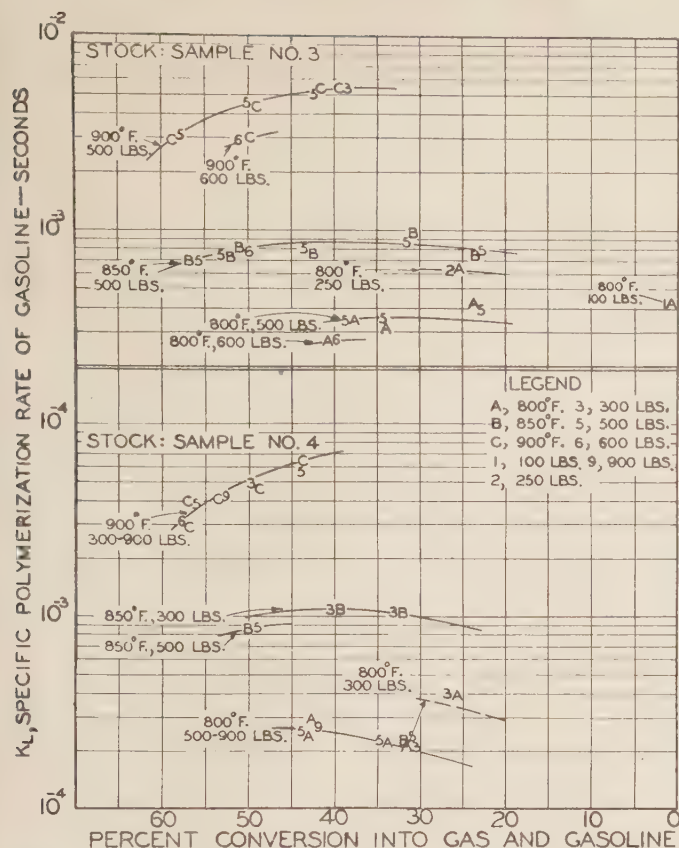


Figure 9. Variation in Specific Rate of Polymerization of Gasoline with Conversion

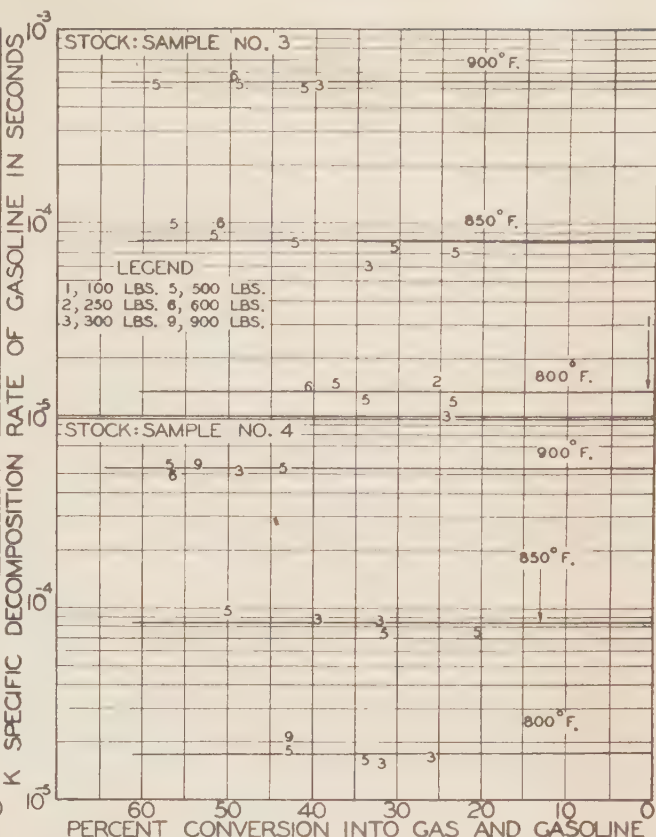


Figure 10. Specific Decomposition Rate of Gasoline vs. Conversion

which shows the rate of gas production as a function of the rate of decomposition of the material, A_G , heavier than gasoline and the gasoline, and the specific rate of polymerization of the gas.

Combining Equations 8, 9, and 10:

$$K_4 = K_1/LA_0[e^{-K_1t} - e^{-(K_1+K_2)t}] \quad (11)$$

The values of K_4 evaluated from the experimental data by Equation 11 are plotted in Figure 10, which shows that the specific rate of decomposition of gasoline is virtually independent of conversion. The values for K_4 are included in Figure 7. The energy of activation for the decomposition of gasoline into gas from Equation 2 and Figure 10 is 72,100 calories, or approximately the value for the rupture of the carbon-carbon linkage obtained by Pease (9).

SPECIFIC RATE OF COKE FORMATION. Owing to the scarcity of data obtained under varied conditions of time, temperature, and pressure for different stocks, and the attendant difficulty in evaluating the amount of materials polymerizable to coke, no attempt has been made to determine quantitatively the specific rate of coke formation. But from the discussion on the effect of time, temperature, and pressure, it may be predicted that the specific rate of coke formation will be increased either by an increase in temperature or by a decrease in pressure in mixed-phase processes as is the specific polymerization rate of gasoline. The specific rate of coke formation under a constant temperature and pressure will increase from a low value at a low percentage conversion into gas and gasoline to a higher value at higher percentage conversion. As the percentage conversion is further increased by prolonged heating, the specific rate of coke formation may decrease from a maximum. The fact that high-temperature and short-time operations give a low yield of coke indicates that the specific rate of coke formation may have a lower temperature coefficient than that for the specific cracking rate of gas and gasoline production.

CONCLUSIONS

1. An increase in temperature increases all the reaction rates involved. In general, an increase in temperature increases the ultimate yield of the volatile materials more than the yields of heavy polymers and coke.
2. An increase in pressure results in a decrease in the rate of polymerization and coke formation in mixed-phase processes. An increase in pressure materially reduces the ultimate yield of coke produced from polymerization at the same percentage conversion.
3. An increase in percentage conversion increases the proportion of gas and coke formed, but decreases the proportion of gasoline and other light liquid fractions produced.
4. The character of charging stock not only influences decomposition but also influences polymerization and coke formation. From the viewpoint of keeping low the ratios of both gas to gasoline and coke to gasoline, for the partially cracked stock of wide and low boiling range, high temperature under high pressure operation at low percentage conversion seems most desirable; for virgin close-cut fractions, high pressure coupled with moderate temperature and percentage conversion appears to be most favorable.

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